

## **General Disclaimer**

### **One or more of the Following Statements may affect this Document**

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

(NASA-CR-169309) PARAMETERS OF CO<sub>2</sub> BANDS  
NEAR 3.6 MICRONS (Ohio State Univ.,  
Columbus.) 21 p HC A02/MF A01 CSCL 07D

N82-32438

G3/25      Unclass  
28897

Parameters of CO<sub>2</sub>

Bands Near 3.6 $\mu$ m\*

M. L. Hoke ✓

J. H. Shaw

Department of Physics

The Ohio State University

Columbus Ohio 43210



\*This work was supported in part by NASA Grant NSG-7469.

### Abstract

The intensities, widths, and positions of lines of three CO<sub>2</sub> bands near 2750 cm<sup>-1</sup> have been determined. The results are in general agreement with other measured and estimated values.

## Introduction

A group of  $\text{CO}_2$  bands near  $2600\text{cm}^{-1}$  has recently been investigated by the nonlinear, least-squares method (NLLS) of whole-band analysis.<sup>1,2</sup> The spectra of a similar set of bands near  $2750\text{cm}^{-1}$ , shown in Fig. 1, have also been analyzed by this technique. These spectra were obtained by coadding 750 interferograms collected by a Nicolet Fourier transform spectrometer. No apodization was applied to the composite interferograms before transformation. The SNR of the upper spectrum, Spectrum I, is about 600 and that of the lower spectrum, Spectrum II, is about 350. The spectral resolution of both is about  $0.07\text{cm}^{-1}$ . Spectrum I was obtained with a path length of 476m through a naturally-occurring sample of  $\text{CO}_2$  at a pressure of 177 torr and a temperature of 294K. A path length of 994m at 741 torr and 292K was used to obtain Spectrum II.

The descriptions of the  $\text{CO}_2$  bands in Table 1 were obtained from the work of Rothman and Young.<sup>3</sup> The strongest band in Table 1 is about ten times weaker than the corresponding band near  $2614\text{cm}^{-1}$ . Thus, although reasonable values for the widths of the lines near  $2600\text{cm}^{-1}$  have been obtained from previous analyses<sup>1</sup> of these bands in Spectrum I, accurate line widths could not be obtained from the upper spectrum in Fig. 1 although the positions of the lines could be well-determined. Estimates of the line widths were obtained from Spectrum II, although these lines are too wide to allow their positions to be determined as precisely as those in Spectrum I.

Lines of all three bands are present in these spectra. Information from approximately 100 lines of band I, sixty lines of band II, and 40 lines of the subbands of band III, most of which are unresolved, contributed to the analysis.



## Spectral Analysis

The method of analysis and the models used to describe the spectra are very similar to those used previously.<sup>1,2</sup>

The vibration-rotation, energy-level models and the expressions for the relative intensities of the CO<sub>2</sub> bands have been described by Rothman and Young.<sup>3</sup> We were able to determine band origins for all of the bands in Table 1. In addition, the quantities B'', D'', B' and D' were estimated for band I, and by fixing B'' and D'' to the values reported by Guelachvili,<sup>4</sup> estimates of B' and D' for the upper state of band II were obtained. However, only the sums B' + B'' were obtained for the subbands of band III.

The term  $(1 + \xi m)^2$  was used to describe the influence of vibration-rotation interactions on CO<sub>2</sub> line intensities. The value of  $\xi$  obtained for the strongest band was less than the standard deviation of  $10^{-3}$ ; no attempt was made to estimate  $\xi$  for the other bands.

The profiles of the lines were found to be adequately described by the Lorentz shape and the  $|m|$ -dependence of the widths was described by the expression of Winters et al.<sup>5</sup>

$$\alpha|m| = W_1 + W_2 \exp[-W_3|m|] + W_4|m| \exp[-B''|m|(|m|-1)/kT]. \quad (1)$$

This expression, which has four adjustable parameters, described the  $|m|$  dependence of the CO<sub>2</sub> lines near 2600cm<sup>-1</sup> satisfactorily.<sup>(1)</sup>

The influence of instrumental effects due to the finite optical-path-difference, the finite source size, and due to residual phase error<sup>6,7</sup> on the spectra were included by using the models described by Hoke.<sup>8</sup> In those cases where they could be compared, the parameter values in these models agreed with those obtained from other analyses.<sup>1,7,8</sup>

The influence of continuous absorption by the wings of distant CO<sub>2</sub> bands

ORIGINAL PAGE IS  
OF POOR QUALITY

Table 1. The band origins, identifications, and intensities of CO<sub>2</sub> bands between 2700 and 2800cm<sup>-1</sup> from the tabulation of Rothman and Young (Ref. 3).

Band	Band Center (cm <sup>-1</sup> )	Molecule	Transition	Band Intensity <sup>a</sup> (10 <sup>24</sup> cm <sup>-1</sup> /mol cm <sup>-2</sup> )
I	2757.229	628	20001-00001	2.20
II	2776.000	627	20001-00001	0.23
III	2791.616	628	21101-01101	0.15

<sup>a</sup>These band intensities were obtained by assuming the isotopic abundances in naturally-occurring CO<sub>2</sub>.

## Rotational Constants

Four sets of rotational constants for band I are given in Table 2, together with experimental values obtained by Guelachvili,<sup>4</sup> and Hoke and Shaw,<sup>2</sup> and values estimated by Chedin<sup>9</sup> and Rothman and Young.<sup>3</sup> The experimental values<sup>2,4</sup> were obtained from other band systems. The ranges of values reported by Hoke and Shaw<sup>2</sup> are caused by correlations among the rotational constants and other retrieved parameters and also by the non-uniqueness of NLLS solutions.

Two sets of constants are reported from each spectrum. In one case, the B" and D" values were retrieved from the spectra and, in the other case, these were fixed to the values of Guelachvili.<sup>4</sup> As in the previous analysis of the corresponding band at  $2614\text{cm}^{-1}$ , it was found that the retrieved values of B" were consistently smaller than that reported by Guelachvili<sup>4</sup> and that the SDR obtained with B" fixed was always smaller than that obtained by retrieving B".

The standard deviations in Table 2 were obtained from the analysis and, as noted previously,<sup>2</sup> they are often optimistically small. The estimated correlation coefficients between the retrieved parameters are also obtained. These show variations from retrieval to retrieval but the correlations between the parameters in Table 2 agree, in both their relative values and absolute magnitudes, with those which would be obtained by performing a linear, least-squares analysis of the line positions.<sup>10</sup>

The largest SDR value was obtained for retrieval A in Table 2. The differences in the line positions calculated from these parameters and the other sets of parameters are shown in Fig. 3. For  $|m| < 50$ , all the line positions obtained from the retrieved parameter sets are consistent to  $\pm 0.003\text{cm}^{-1}$ . Although the line positions obtained from the spectrum of the higher pressure sample are less precise than those obtained from spectrum I the results confirm the conclusions of Freed et al.<sup>11</sup> and of Hollins and Jordan<sup>12</sup> that the pressure shifts of infrared

CO<sub>2</sub> lines are small compared with their widths.

The lines of the <sup>16</sup>O<sup>12</sup>C<sup>17</sup>O band are much weaker than those of band I and the upper state constants B' and D', given in Table 3, were obtained by fixing B'' and D''. These sets of constants give positions of lines with |m| < 35 which agree within  $\pm 0.005\text{cm}^{-1}$ . This is less than one tenth of the observed line width.

Information about the weakest of the bands was only obtained from spectrum II. Initial estimates of the rotational constants were obtained by calculating the spectrum of bands I and II only and subtracting this from the observed spectrum. Many of the lines of band III, including the Q branch could then be seen. Since the lines of the two subbands were only resolved for |m| > 15 it was not possible to obtain satisfactory individual B' and B'' values in the subsequent NLLS analysis.

Absolute values for the band origins were obtained by calibrating the spectra against the previously-measured positions<sup>13,14</sup> of water vapor lines present in the spectra. The estimated accuracy of the band origins<sup>15</sup>,  $\pm 2 \times 10^{-3}\text{cm}^{-1}$ , is smaller than the precision, about  $10^{-4}\text{cm}^{-1}$ , estimated by the NLLS analyses. These band origins are compared with those of Rothman and Young<sup>3</sup> and Chedin<sup>9</sup> in Table 4.

#### Line Widths

It was assumed that the corresponding lines in each of the bands had the same width and all the widths were reduced to standard conditions of 296K, 760 torr by the relation

$$\alpha(|m|, P, T) = \alpha(|m|, P_0, T_0) (P/P_0) (T_0/T)^{1/2}. \quad (2)$$

The widths obtained from spectrum II are compared with those obtained from the previous analyses of the bands near  $2600\text{cm}^{-1}$  in Fig. 4. In both cases the dominant band is due to <sup>16</sup>O<sup>12</sup>C<sup>18</sup>O and the broadening is due to the isotope <sup>12</sup>C<sup>16</sup>O<sub>2</sub>. The precision of each set of results is estimated to be about 2-3%.

Since the maximum difference between the two sets of widths is less than 4% the effects due to differences in the vibrational transitions involved are small. The values of the constants  $W_1$  in Eq. (1), which are given in Table 5, are those which produced the curves in Fig. 4. They were obtained from the solutions with the largest SDRs. Other sets of values of  $W_1$ , obtained from retrievals with almost equally good fits to the experimental data, gave curves almost identical to that shown in Fig. 5, even though the values of the constants differed by several times the standard deviations given in Table 5. This behavior is consistent with that found for most of the other parameter values.<sup>1,2</sup>

#### Intensities

The band sums, the sums of the intensities of all the lines in each band, were calculated as described previously.<sup>1</sup> The values in Table 6 were obtained from the analysis with the largest SDR. The spreads obtained from almost equally good retrievals are also given together with the values estimated by Rothman and Young.<sup>3</sup> These spreads are an order of magnitude larger than the standard deviations obtained by the NLLS analyses. The results for bands II and III were obtained only from spectrum II and, in order to obtain band sum III, it was necessary to fix the sums  $B' + B''$ . The experimental intensities for two of the bands are significantly larger than those estimated by Rothman and Young.<sup>3</sup>

#### Conclusions

The values for the band sum, the line widths, and the rotational parameters of band I have been obtained with accuracies sufficient for use in most atmospheric transmittance calculations. The corresponding values for bands II and III describe the experimental data available adequately. The results are in satisfactory agreement with the previous measurements of Guelachvili<sup>4</sup> and Hoke and Shaw<sup>1,2,8</sup> and with the estimates of Rothman and Young.<sup>3</sup>



## References

1. M. L. Hoke and J. H. Shaw, "Analysis of  $\text{CO}_2$  bands near  $2600\text{cm}^{-1}$ ," *Appl. Opt.*, 21, 929 (1982).
2. M. L. Hoke and J. H. Shaw, "Rotational analysis of  $\text{CO}_2$  bands near  $4\mu\text{m}$ ," *Appl. Opt.*, 21, 935 (1982).
3. L. S. Rothman and L. D. S. Young, "Infrared energy levels and intensities of carbon dioxide-II," *Jour. Quant. Spectrosc. Radiat. Transfer*, 25, 505 (1981).
4. G. Guelachvili, "High resolution Fourier spectra of carbon dioxide and three of its isotopic species near  $4.3\mu\text{m}$ ," *J. Mol. Spec.*, 79, 72 (1980).
5. B. H. Winters, S. Silverman, and W. S. Benedict, "Line shape in the wing beyond the band head of the  $4.3\mu$  band of  $\text{CO}_2$ ," *Jour. Quant. Spectrosc. Radiat. Transfer*, 4, 527 (1964).
6. G. A. Vanasse and H. Sakai, "Fourier Spectroscopy" in "Progress in Optics, Vol. VI," E. Wolf ed., North-Holland, Amsterdam (1967).
7. C. R. Anderson and D. R. Mattson, "Phase correction techniques in Fourier transform-infrared (FT-IR)," *Soc. Photo-Opt. Instru. Eng.* 289, 199 (1981).
8. M. L. Hoke "Analysis of  $\text{CO}_2$  bands near  $2600\text{cm}^{-1}$ ," Ph.D diss. Ohio State Univ. (1982).
9. A. Chedin, "The carbon dioxide molecule," *J. Mol. Spec.*, 76, 430 (1979).
10. D. L. Albritton, A. L. Schmeltekopf and R. N. Zare, "An introduction to the least-squares fitting of spectroscopic data" in "Modern Spectroscopy. Modern Research II," K. Narahari Rao, ed., Academic Press New York (1966).
11. C. Freed and R. G. O'Donnell, "Advances in  $\text{CO}_2$  laser stabilization using the  $4.3\mu\text{m}$  fluorescence technique" *Metrologia*, 13, 151 (1977).
12. R. C. Hollins and D. L. Jordan, "Pressure shift in an atmospheric pressure  $\text{CO}_2$ ,  $\text{N}_2$ , He gas mixture," *J. Phys. B.* 15, L 491 (1982).

13. L. A. Pugh, Ph.D dissertation, "A detailed study of the near infrared spectrum of water vapor," Ohio State University (1972).
14. C. Camy-Peyret and J. M. Flaud, "Line positions and intensities in the  $\nu_2$  band of  $\text{H}_2^{16}\text{O}$ ," Mol. Phys., 32, 523 (1976).
15. R. L. Hawkins, M. L. Hoke, and J. H. Shaw "Wavenumber calibration of Fourier transform spectra," Appl. Spectrosc. (accepted).

ORIGINAL PAGE IS  
OF POOR QUALITY

Table 1. The band origins, identifications, and intensities of CO<sub>2</sub> bands between 2700 and 2800cm<sup>-1</sup> from the tabulation of Rothman and Young (Ref. 3).

Band	Band Center (cm <sup>-1</sup> )	Molecule	Transition	Band Intensity <sup>a</sup> (10 <sup>24</sup> cm <sup>-1</sup> /mol cm <sup>-2</sup> )
I	2757.229	628	20001-00001	2.20
II	2776.000	627	20001-00001	0.23
III	2791.616	628	21101-01101	0.15

<sup>a</sup>These band intensities were obtained by assuming the isotopic abundances in naturally-occurring CO<sub>2</sub>.



Table 2. Rotational constants for Band I (20001-00001,628) obtained in this work and in other studies.

Retrieval	Spectrum	SDR	$B''$ ( $\text{cm}^{-1}$ )	$B'$ ( $\text{cm}^{-1}$ )	$10^3 D''$ ( $\text{cm}^{-1}$ )	$10^3 D'$ ( $\text{cm}^{-1}$ )
A	I	400	0.36818277(56)	0.36903714(22)	12.130(37)	8.882(36)
B	I	392	0.36818571 <sup>a</sup>	0.369036189(46)	11.9030 <sup>a</sup>	8.494(96)
C	II	170	0.3681616(75)	0.3690155(76)	11.75(35)	8.416(35)
D	II	168	0.36818571 <sup>a</sup>	0.36903951(87)	11.9030 <sup>a</sup>	8.550(52)
			0.36818571(52) <sup>a</sup>		11.9030(186) <sup>a</sup>	
			0.3681771 <sup>b</sup>	0.369039 <sup>b</sup>	11.7 <sup>b</sup>	7.7 <sup>b</sup>
			0.368186 <sup>c</sup>	0.369024 <sup>c</sup>	11.9 <sup>c</sup>	8.8 <sup>c</sup>
			0.36816235(22) <sup>d</sup>		11.5660(49) <sup>d</sup>	
			0.36818571 <sup>a,d</sup>		12.413(18) <sup>d</sup>	

<sup>a</sup>Guelachivili (Ref. 4)

<sup>b</sup>Rothman and Young (Ref. 3)

<sup>c</sup>Chedin (Ref. 9)

<sup>d</sup>Range of values obtained by Hoke and Shaw (Ref. 2)

ORIGINAL PAGE IS  
OF POOR QUALITY

Table 3. Upper State Rotational Constants for Band II (20001-0001,627).

Source	$B'$ ( $\text{cm}^{-1}$ )	$10^8 D'$ ( $\text{cm}^{-1}$ )
Retrieval $B^\dagger$	0.379172(7)	0.0 <sup>*</sup>
Retrieval $D^\dagger$	0.379327(17)	16.15(12)
Rothman <sup>a</sup>	0.379270	8.8
Chedin <sup>b</sup>	0.379248	9.3

<sup>†</sup> see Table 2 for details

<sup>\*</sup> standard deviation not obtained

<sup>a</sup> (Ref. 3)

<sup>b</sup> (Ref. 9)

ORIGINAL PAGE IS  
OF POOR QUALITY

Table 4. Origins of CO<sub>2</sub> bands between 2700 and 2800 cm<sup>-1</sup>

Band (see Table 2)	Molecule	Rothman and Young (cm <sup>-1</sup> )	Chedin <sup>**</sup> (cm <sup>-1</sup> )	This Work (cm <sup>-1</sup> )
I	628	2757.229	2757.211	2757.183(2)
II	627	2776.000	2775.610	2775.595(2)
III	628	2791.616	2791.593	2791.512(2)

\* Ref. 3

\*\* Ref. 10

Table 5. Best estimates of the parameters of the Winters et al (Ref. 5) model for describing the dependence of CO<sub>2</sub> line widths on  $|m|$ .

Parameter**	Previous work*	This work
$W_1$ (cm <sup>-1</sup> /atm)	$8.34(2) \times 10^{-2}$	$8.0732(8) \times 10^{-2}$
$W_2$ (cm <sup>-1</sup> /atm)	$5.83(6) \times 10^{-2}$	$6.15(4) \times 10^{-2}$
$W_3$	-0.1539(4)	-0.179(9)
$W_4$ (cm <sup>-1</sup> /atm)	$1.82(2) \times 10^{-3}$	$1.89(9) \times 10^{-3}$

\* See Reference 1.

\*\* Corrected to 296 K, 760 torr.

ORIGINAL PAGE IS  
OF POOR QUALITY

Table 6. Band Intensities.

Band	Molecule	Intensity ( $10^{24} \text{ cm}^{-1} / \text{mol cm}^{-2}$ )		
		Rothman and Young <sup>a</sup>	Spectrum I <sup>*</sup>	Spectrum II <sup>*</sup>
I	628	2.20	3.31 (12)	3.28 (12)
II	627	0.23	-	0.214 (12)
III	628	0.15	-	0.255(15)

\* The values in brackets represent the total scatter in the estimated values.

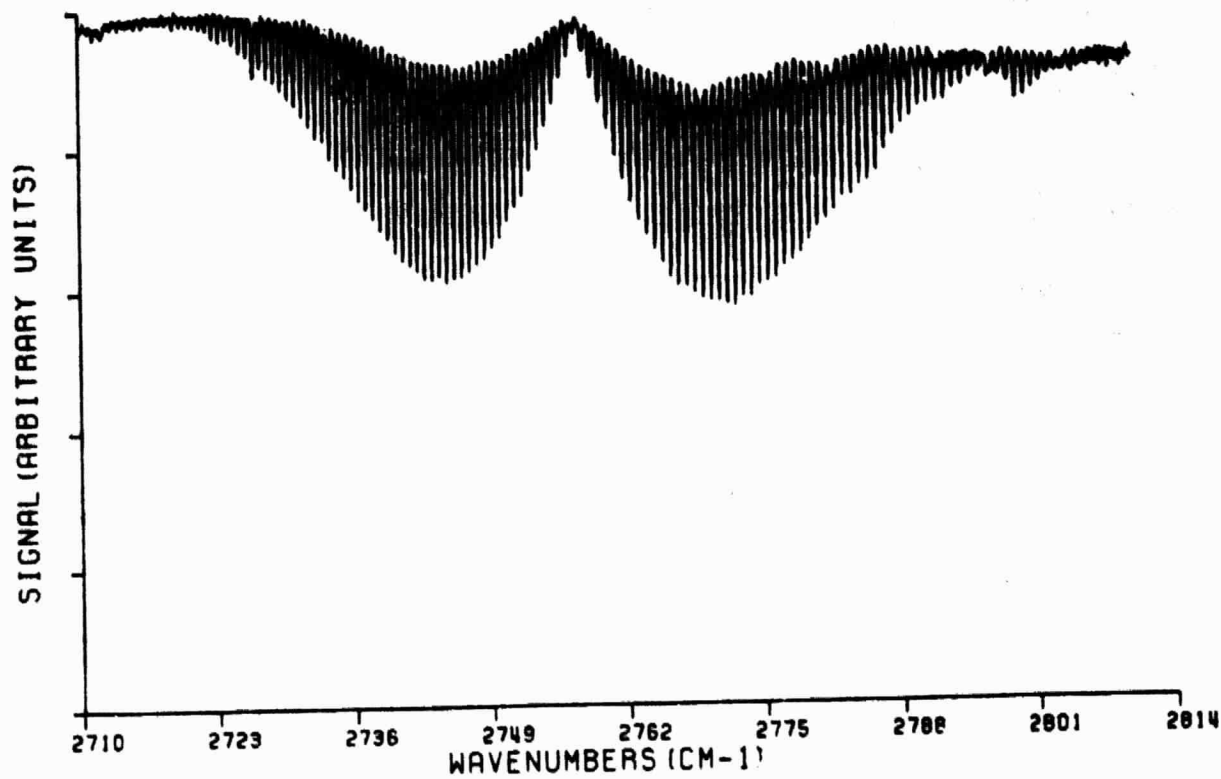
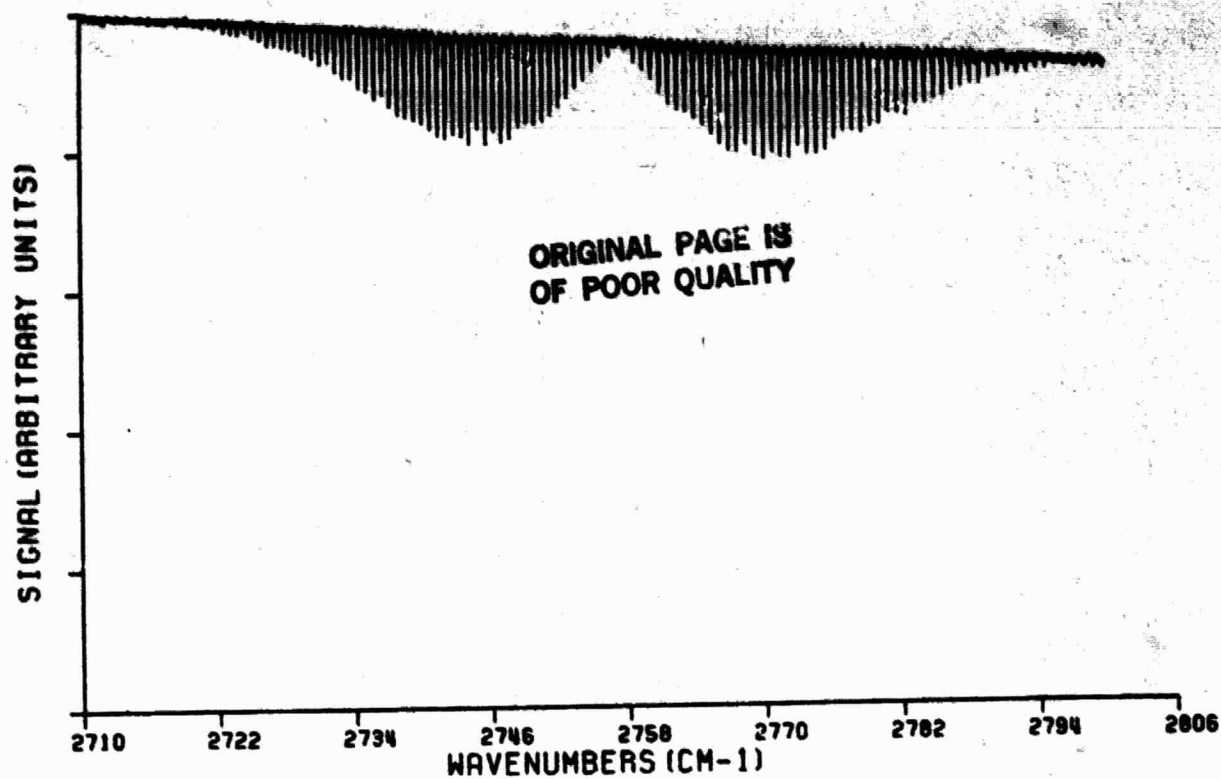
<sup>a</sup>See Ref. 3.

Fig. 1. Top: Spectrum of a 476m path of  $\text{CO}_2$ , pressure 177 torr, temperature 294K; bottom: spectrum of a 994m path of  $\text{CO}_2$ , pressure 741 torr, temperature 292K. These are referred to as Spectrum I and Spectrum II, respectively, in the text.

Fig. 2. Upper left: a portion of Spectrum II in a region where there is little line absorption. Upper right. a portion of the same spectrum. Bottom: the difference between the observed and calculated values, shown on an expanded scale.

Fig. 3. The differences in the line positions calculated from the constants in retrieval A, Table 3 and the positions calculated from the other retrievals (labeled according to the retrieval identification in Table 3), including those calculated from the constants of Rothman and Young (R) and Chedin (Ch).

Fig. 4. The  $|m|$  dependence of the widths of  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  lines broadened by  $^{12}\text{C}^{16}\text{O}_2$  (reduced to 296K, 760 torr). The top curve was obtained from the analysis of the 20002-0001 band at  $2614\text{ cm}^{-1}$  (see reference 1). The bottom curve was obtained from the analysis of the 20001-00001 band at  $2757\text{ cm}^{-1}$ .





ORIGINAL PAGE IS  
OF POOR QUALITY

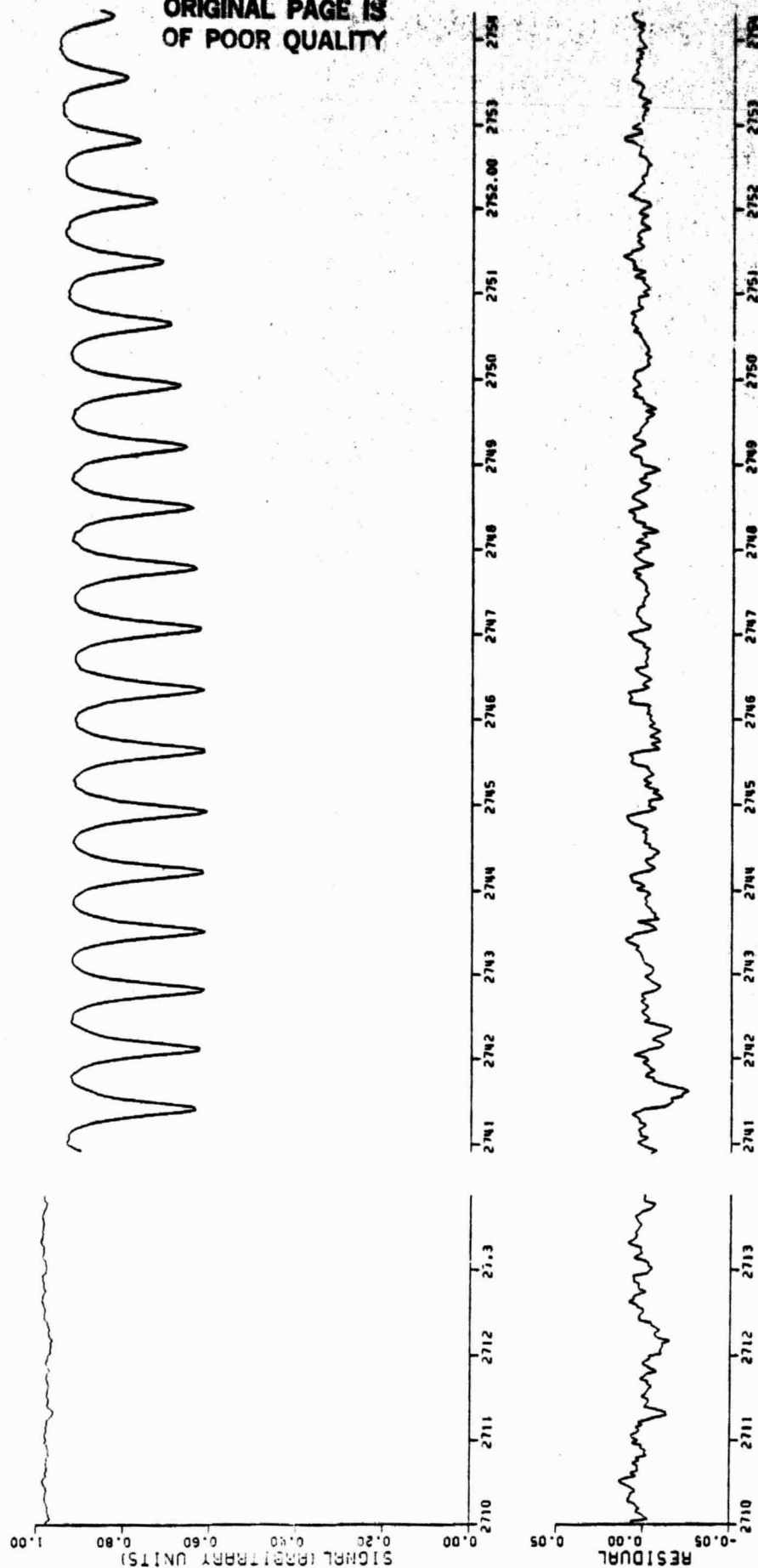


Fig. 2



ORIGINAL PAGE IS  
OF POOR QUALITY

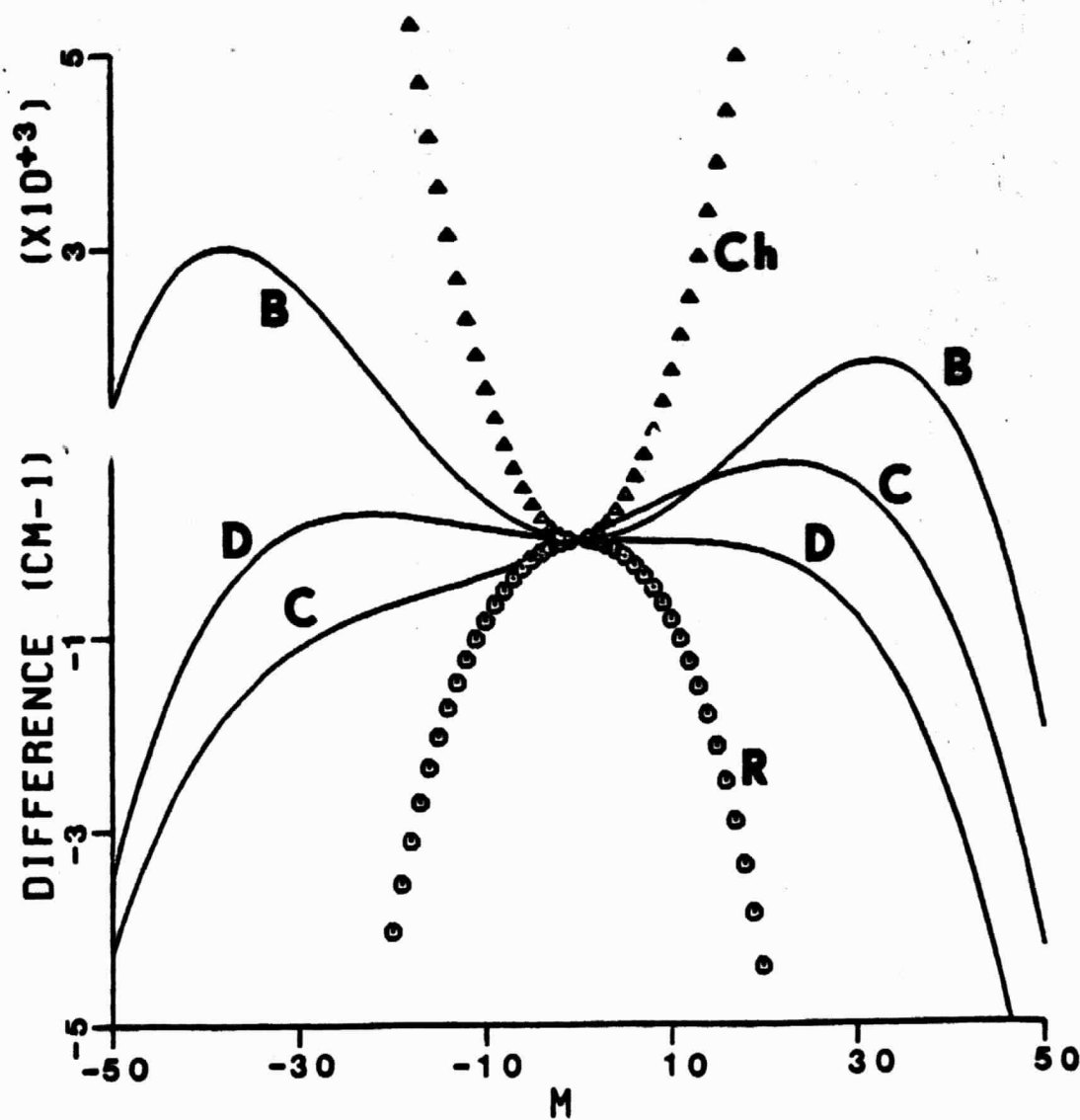


Fig 3

ORIGINAL PAGE IS  
OF POOR QUALITY

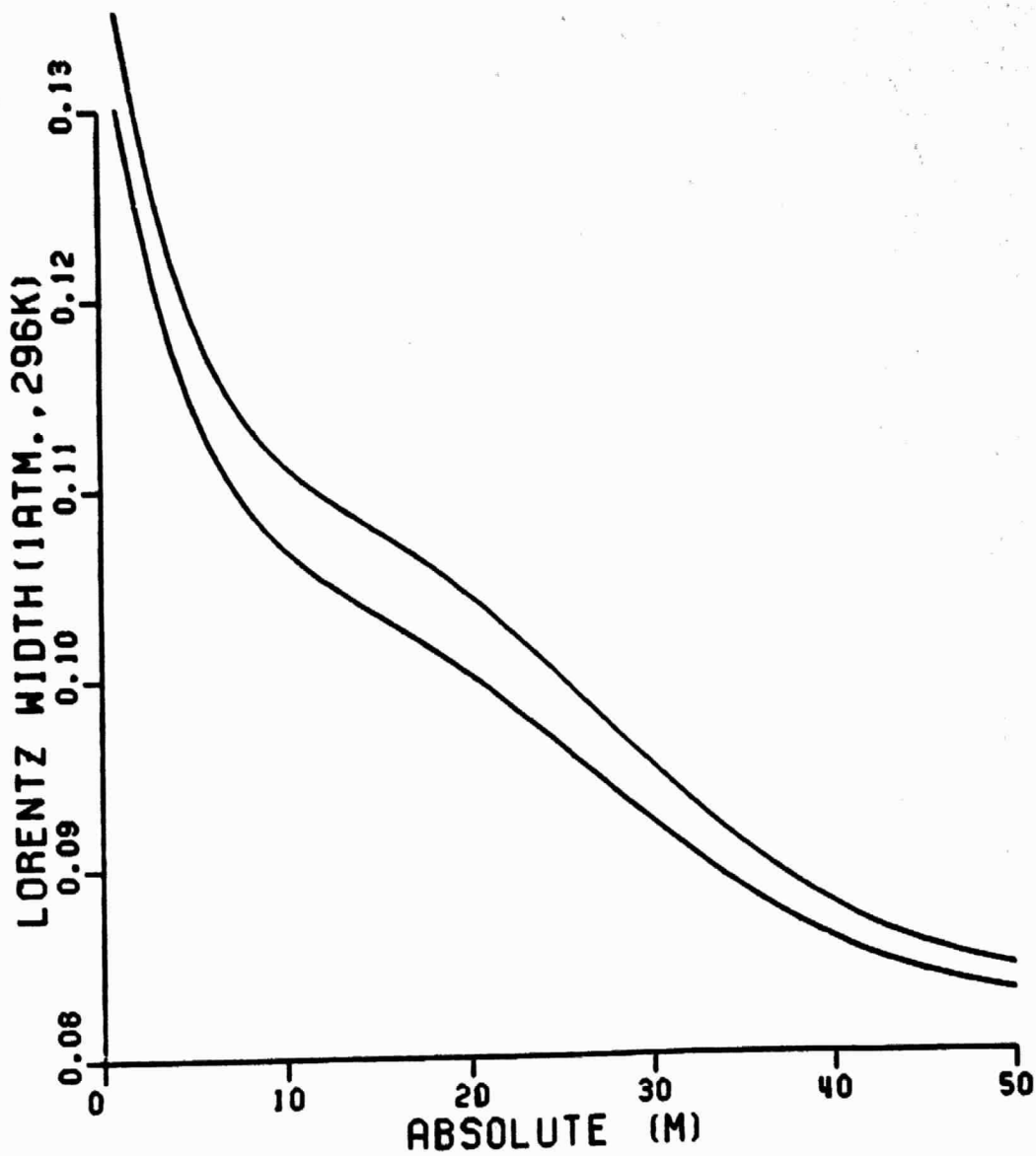


Fig. 4